



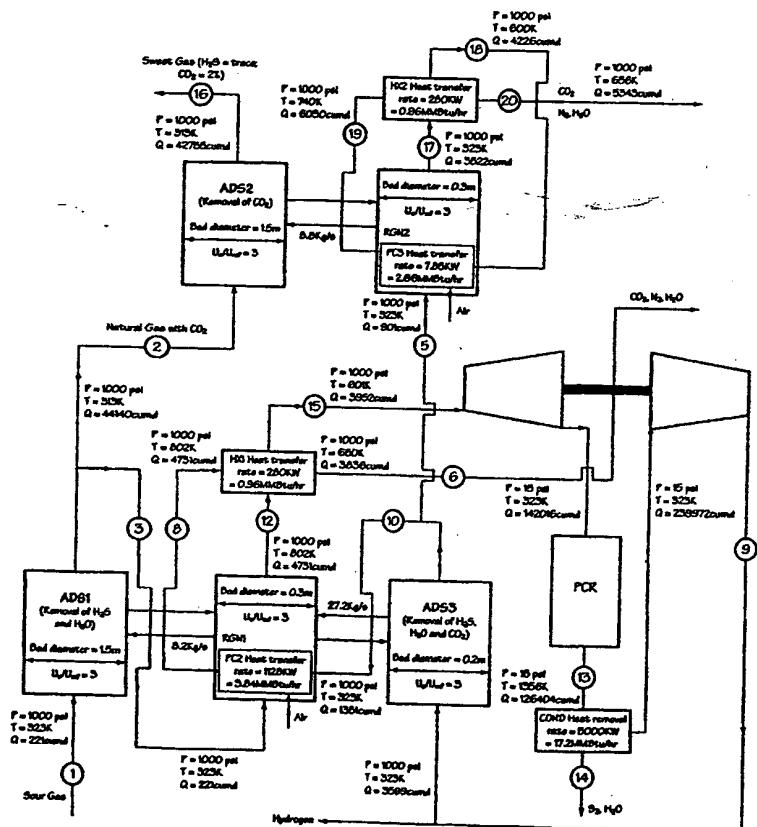
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

SEARCHED UNDER THE PATENT COOPERATION TREATY (PCT)		
(51) International Patent Classification 7 :  B01J 8/18, 8/26, C10L 3/10, H05H 1/00		A1
		(11) International Publication Number:  WO 00/56441
		(43) International Publication Date: 28 September 2000 (28.09.00)
 (21) International Application Number: PCT/US00/07753		
 (22) International Filing Date: 23 March 2000 (23.03.00)		
 (30) Priority Data: 60/125,962 24 March 1999 (24.03.99) US		
 (71) Applicant (for all designated States except US): UNIVERSITY OF WYOMING [US/US]; 16th & Gibbon, Laramie, WY 82071 (US).		
 (72) Inventors; and		
 (75) Inventors/Applicants (for US only): AGARWAL, Pradeep, K. [US/US]; 2121 East Curtis Street, Laramie, WY 82072 (US). LINJEWILE, Temi, M. [TZ/US]; 2250 Coe Street, Apt. 133, Laramie, WY 82072 (US). HULL, Ashley, S. [AU/US]; 205 South 30th Street, Apt. B-12, Laramie, WY 82070 (US).		
 (74) Agent: TRACY, Emery, L.; P.O. Box 1518, Boulder, CO 80306 (US).		
 (81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).		
 Published With international search report.		

(54) Title: SYSTEM FOR RECOVERY OF SULFUR AND HYDROGEN FROM SOLID GAS

### (57) Abstract

A process and apparatus is provided for the removal of contaminants, such as hydrogen sulfide, carbon dioxide and water, out of natural gas (1) is provided. The apparatus comprises a plurality of purifying fluidized beds, each of which contains an adsorbent, such as molecular sieve 5A, and which operates at a temperature ranging from about 20 °C to about 60 °C and removes at least a portion of the hydrogen sulfide and other contaminants from the natural gas so as to provide a purified natural gas (2) and a contaminant loaded adsorbent. The contaminant loaded adsorbent is regenerated in a regenerator unit at a temperature of about 100 °C to about 300 °C to produce a regenerated adsorbent, which is recycled back to a fluidized bed and a hydrogen sulfide rich regeneration off-gas (12), which is injected into a non-thermal plasma reactor that dissociates the hydrogen sulfide into hydrogen and sulfur (13).



$$H_2S = 1\% ; CO_2 = 5\% ; H_{2O} = 0.1 \text{ mol}^{-1} @ 1000 \text{ psia}, 323K; d_T = 1.5 \text{ mm}$$

***FOR THE PURPOSES OF INFORMATION ONLY***

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LJ	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		

## SYSTEM FOR RECOVERY OF SULFUR AND HYDROGEN FROM SOUR GAS

5        The present application is a continuation of pending provisional patent application Serial No. 60/125,962, filed on March 24, 1999, entitled "System For Recovery Of Sulfur And Hydrogen From Sour Gas Using A Plasma Reactor".

### BACKGROUND OF THE INVENTION

10      1. Field of the Invention

This invention relates generally to a process for removal of hydrogen sulfide from a gaseous stream and the subsequent recovery of hydrogen and sulfur from the hydrogen sulfide and, more particularly, it relates to removal of H<sub>2</sub>S, CO<sub>2</sub>, and H<sub>2</sub>O from a sour natural gas stream in a fluidized bed adsorber followed by the conversion of H<sub>2</sub>S to elemental sulfur and hydrogen in a corona reactor.

15      2. Description of the Prior Art

The proven reserves of natural gas in the United States are of the order of 170 trillion cubic feet; taking data from various exploration programs into account, the natural gas resource base may be inferred to be close to 1118 trillion cubic feet. About twenty (20) trillion cubic feet of the proven reserves of natural gas contain significant amounts of H<sub>2</sub>S, CO<sub>2</sub>, and H<sub>2</sub>O and other sulfur-containing contaminants. The sulfur must be removed from such streams to enable users to comply with environmental regulations. Moisture removal is necessary since the presence of moisture leads to the formation of hydrates, which through increasing the pressure drop along the transmission pipeline, decrease transmission capacity. CO<sub>2</sub> is an undesirable diluting gas, which lowers the heating value of natural gas. Presence of moisture and H<sub>2</sub>S is also a major factor in corrosion of equipment.

25      Processes for removal of H<sub>2</sub>S from a gas stream are based on two principal mechanisms: absorption by regenerable solvents and adsorption on a bed of solids. Processes based on absorption often involve the use of one of the several amine solutions such as monethanolamine, diethanolamine, and triethanolamine, followed by thermal regeneration of the solvent to recover acid gases and the amine solution.

30      Most adsorption processes employ fixed beds, but moving and fluidized beds are also used. Adsorbent materials for H<sub>2</sub>S removal include molecular sieves, iron oxide, zinc oxide, zinc titanate, tin oxide, and zinc ferrite. Molecular sieves have excellent selective

mercaptan. Since molecular sieves are designed to strongly attract and retain specific gas components, they are well suited for thermal-swing regeneration in a temperature swing adsorption cycle. Regeneration produces an enriched stream of the adsorbate and a revitalized sorbent for reuse.

5       Conversion of hydrogen sulfide to recover sulfur is often accomplished via the Claus process. The Claus process was invented in 1883 by Carl Friedrich Claus, a London Chemist, and was put into industrial-scale operation in the 1950's in the United States. A typical Claus sulfur-recovery plant consists of two major process stages. Stage one consists of a combustion furnace, waste heat boiler, and a sulfur condenser. Stage two is  
10      comprised of a series of catalytic converters numbering between one and four units. Each of the catalytic converters is equipped with a re-heating unit, catalyst bed, and a sulfur condenser. Hydrogen sulfide is converted to sulfur in the Claus process by two principal reactions: combustion of part of the hydrogen sulfide to sulfur dioxide and subsequent reaction of sulfur dioxide with hydrogen sulfide over a catalyst to produce sulfur and  
15      water.



Sulfur recovery up to 97% is achievable by employing multiple catalytic converters.

20      Conversion of  $\text{H}_2\text{S}$  to elemental sulfur can also be achieved by dissociation of  $\text{H}_2\text{S}$  by energetic electrons. This can be implemented by employing a number of nonthermal plasma processes, which include corona, dielectric barrier, microwave, and radio-frequency discharges. In a pulsed corona reactor, high-voltage pulses produce short-lived microdischarges, which preferentially accelerate the electrons without imparting significant energy to the ions. This results in improvement in power consumption and energy saving potential. In addition, since most of the energy applied goes to accelerating the electrons rather than the massive ions, larger reactor volumes are possible because the high energy electrons are capable of filling larger volumes.  
25

Existing methods for removal of  $\text{H}_2\text{S}$  by adsorption use fixed bed technology. Fixed beds suffer from the inherent problem of slow response to changes in gas  
30      temperature. By comparison, fluidized-bed adsorption processes offer excellent gas-solid contact, fast kinetics, and steady operation. However, stresses induced by rapid temperature swings and fluidization have hampered efforts to use fluidized beds for adsorption.

Most industrial sulfur recovery processes are based on the Claus process,

which entails partial combustion of H<sub>2</sub>S stripped from the natural gas stream to form SO<sub>2</sub>, Reaction (1). Elemental sulfur is recovered by the reaction of the remaining H<sub>2</sub>S with SO<sub>2</sub> as shown in Reaction (2). Thermodynamic constraints of Reaction (2) limit the conversion of H<sub>2</sub>S in a single stage catalytic converter (to about 0.7) and, hence, the thermal recovery of elemental sulfur from the Claus furnace (operated at around 2400° F). In order to increase the efficiency of sulfur recovery, the effluent gases from the Claus furnace are cooled to recover sulfur and then contacted over a number of packed-bed catalytic converters at lower temperatures. Depending on the number of stages employed, recovery efficiencies vary between 90% and 98%. For optimum operation, the composition of the gases in the Claus process must be maintained such that the H<sub>2</sub>S/SO<sub>2</sub> ratio is 2:1. Even after several conversion stages, 2000-3000 ppm of H<sub>2</sub>S and SO<sub>2</sub> may remain in the effluent gas from the Claus process, posing environmental compliance problems. Customarily, an additional tailgas cleanup unit is employed to ensure that the final overall sulfur recovery exceeds 99%. Two such processes for tailgas cleanup are the Shell Claus off-gas treatment (SCOT) process and the Superclaus process. The SCOT tailgas cleanup process is the most widely used. However, an "add-on" SCOT plant may cost as much as the parent Claus plant itself.

Alternatively, a Superclaus unit may be introduced as the last stage in the series of catalytic converters. The process is based on selective oxidation of the unconverted H<sub>2</sub>S to elemental sulfur, in the presence of a catalyst. Although both SCOT and Superclaus processes can improve sulfur recovery efficiency, the cost of installation of plant may not be offset by the sulfur recovered. Moreover, both processes fail to recover hydrogen, a valuable resource that may improve the overall economics of sulfur removal.

The mechanism of electron-impact assisted dissociation of H<sub>2</sub>S occurs according to the following reactions:



Unstable atomic sulfur and hydrogen formed in reaction (3), recombine to stable H<sub>2</sub> and S as shown in reactions (4) and (5). In an electrical discharge reactor, the reactivation of H<sub>2</sub> and S leads to reformation of H<sub>2</sub>S. This has an impact on the conversion and energy efficiency of the process.

SUMMARY

The present invention is a device for removing contaminants from a natural gas stream. The device comprises first adsorbent means positioned within a first fluidized bed operating at a first predetermined temperature for removing at least a portion of the contaminants from the natural gas stream and creating a partially sweetened natural gas stream. Second adsorbent means are positioned within a second fluidized bed operating at a second predetermined temperature for receiving the partially sweetened natural gas stream with the second adsorbent means removing at least a portion of the contaminants from the partially sweetened natural gas stream.

In an embodiment of the present invention, the contaminants are selected from the group consisting of H<sub>2</sub>S, CO<sub>2</sub>, and H<sub>2</sub>O. Furthermore, preferably, the first adsorbent means is a molecular sieve and the second adsorbent means is a molecular sieve.

In another embodiment of the present invention, the first predetermined temperature is greater than the second predetermined temperature. Preferably, the first predetermined temperature is between approximately twenty (20°) degrees C and approximately sixty (60°) degrees C and the second predetermined temperature is between approximately one hundred (100°) degrees C and approximately three hundred (300°) degrees C.

In still another embodiment of the present invention, the device further comprises conversion means for converting H<sub>2</sub>S within the removed contaminants to elemental sulfur and hydrogen at a predetermined temperature less than approximately four hundred (400°) degrees C. Preferably, conversion means is a nonthermal plasma corona reactor.

The present invention additionally includes an apparatus for converting H<sub>2</sub>S to elemental sulfur and hydrogen. The apparatus comprises conversion means for receiving H<sub>2</sub>S and for converting H<sub>2</sub>S to elemental sulfur and hydrogen at a predetermined temperature less than approximately four hundred (400°) degrees C.

In an embodiment of the present invention, the conversion means is a nonthermal plasma corona reactor.

In still another embodiment of the present invention, the apparatus further comprises adsorbent means positioned within a fluidized bed for removing at least a portion of H<sub>2</sub>S from a natural gas stream and means for providing the removed H<sub>2</sub>S to the conversion means.

In yet another embodiment of the present invention, the adsorbent means

includes a first adsorbent having a first predetermined temperature and second adsorbent having a second predetermined temperature. Preferably, the first adsorbent means and the second adsorbent means are molecular sieves. Furthermore, preferably, the first predetermined temperature is greater than the second predetermined temperature.

5       The present invention further includes a method for removing H<sub>2</sub>S and other contaminants from a natural gas stream and converting H<sub>2</sub>S to elemental sulfur and hydrogen. The method comprises providing a first adsorbent, positioning the first adsorbent within a fluidized bed at a first predetermined temperature, introducing the natural gas stream to the first adsorbent thereby removing at least a portion of the H<sub>2</sub>S and other contaminants from the natural gas stream and creating a partially sweetened natural gas stream, providing a second adsorbent, positioning the second adsorbent within a fluidized bed at a second predetermined temperature, introducing the partially sweetened natural gas stream to the second adsorbent thereby removing at least a portion of the contaminants from the partially sweetened natural gas stream, providing a nonthermal plasma reactor, introducing the removed contaminants to the nonthermal plasma reactor, and converting the H<sub>2</sub>S to elemental sulfur and hydrogen at a third predetermined temperature.

10

15

In an embodiment of the present invention, the first adsorbent means and the second adsorbent means are molecular sieves. Preferably, the first predetermined temperature is greater than the second predetermined temperature with the first predetermined temperature being between approximately twenty (20°) degrees C and approximately sixty (60°) degrees C and the second predetermined temperature being between approximately one hundred (100°) degrees C and approximately three hundred (300°) degrees C. Furthermore, preferably, the third predetermined temperature being less than approximately four hundred (400°) degrees C.

20

25

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view illustrating a system for recovery of sulfur and hydrogen from sour gas, constructed in accordance with the present invention, including (1) removal of H<sub>2</sub>S, CO<sub>2</sub>, and H<sub>2</sub>O from a sour natural gas stream and sorbent regeneration and (2) conversion of H<sub>2</sub>S to elemental sulfur and hydrogen in a corona reactor; and

30

FIG. 2 is a schematic diagram illustrating the process for (1) removal of H<sub>2</sub>S, CO<sub>2</sub>, and H<sub>2</sub>O from a sour natural gas stream and sorbent regeneration and (2) conversion of

H<sub>2</sub>S to elemental sulfur and hydrogen in a corona reactor, constructed in accordance with the present invention.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As can be understood by those persons skilled in the art, the basic concepts of the present invention can be embodied in a variety of ways. The present invention involves both processes and devices to accomplish the improved processes. In the present application, the processes are discussed in detail. Systems and devices to be established under the invention are described as items inherent to utilization of such processes. To the extent some devices are disclosed, it should be understood that these not only accomplish certain methods, but also can be varied in a number of ways. Importantly, as to all of the foregoing, all of these facets should be understood to be encompassed by the disclosure herein.

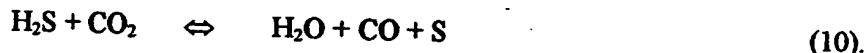
As illustrated in FIG. 1, the present invention comprises the removal of H<sub>2</sub>S, CO<sub>2</sub>, H<sub>2</sub>O, and other sulfur-containing contaminants from natural gas streams employing a fluidized bed adsorber and recovery of elemental sulfur and hydrogen in a corona reactor at low temperatures, preferably less than approximately four hundred (400°) degrees C. The process consists of two steps. The first step is the removal of H<sub>2</sub>S, CO<sub>2</sub>, and H<sub>2</sub>O from a sour natural gas stream and sorbent regeneration. This step is accomplished using the concept of temperature swing adsorption. The contaminants in the natural gas are adsorbed on molecular sieves in fluidized beds operated at low temperatures, preferably between approximately twenty (20°) degrees C and approximately sixty (60°) degrees C. The spent sorbent is circulated to a high temperature, preferably between approximately one hundred (100°) degrees C and approximately three hundred (300°) degrees C, fluidized bed regenerator and the gas stripped from the sorbent in the regenerator is used for sulfur and hydrogen recovery.

The second step is the conversion of H<sub>2</sub>S to elemental sulfur and hydrogen in a corona reactor at a temperature less than approximately four hundred (400°) degrees C. The H<sub>2</sub>S, CO<sub>2</sub>, and CH<sub>4</sub> from the regenerator will form the primary feed to a corona reactor. Recovery of elemental sulfur and hydrogen from H<sub>2</sub>S in a nonthermal plasma reactor is based, primarily, on the following reactions:





The emphasis is on the dissociation of  $\text{H}_2\text{S}$  according to Reaction (6). Formation of sulfur occurs by Reaction (7). Reactions (8) and (9) are responsible for formation of hydrogen. Since the feed gas stream to the corona reactor consists of  $\text{H}_2\text{S}$  and  $\text{CO}_2$ , the following reaction can also take place:



The approach herein has a distinct advantage in that the fuel value of  $\text{H}_2\text{S}$  is transformed to CO and  $\text{H}_2$ ; this synthesis gas can actually be burnt to meet the energy requirements of the process. While  $\text{CO}_2$  also leads to the formation of COS, its production can be minimized by choice of proper operating conditions.

Referring now to FIG. 2, the processes of sweetening sour gas and recovery of sulfur and hydrogen are integrated into a single compact process, as described below. First, the sour natural gas stream is contacted with the adsorbent (such as a molecular sieve 5A) in a fluidized bed adsorber, designated as ADS1 in FIG. 2, to effect the removal of  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{O}$ , and other sulfur-containing contaminants. The partially sweetened natural gas stream is then passed through a second fluidized bed adsorber, designated as ADS2, where  $\text{CO}_2$  is stripped, also, using the molecular sieve 5A as an adsorbent. Though, in principle,  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and other sulfur-containing contaminants can all be removed from the natural gas stream by the molecular sieve 5A in a single adsorber unit, two separate units become necessary for maximizing the process efficiency for sulfur recovery.

The sequential stripping of  $\text{H}_2\text{S}$  and  $\text{H}_2\text{O}$  in ADS1 followed by removal of  $\text{CO}_2$  in ADS2 is made possible by the well-defined sequence in which these species are adsorbed on the molecular sieve. The residence time and the circulation rates of solids, then will be controlled so that the species adsorbed in ADS1 are primarily  $\text{H}_2\text{S}$  and  $\text{H}_2\text{O}$ .

At a high operating pressure (e.g., 1000 psig), the fluidized bed adsorber units can be operated in a bubbling bed mode. Calculations show that these adsorber units can be very compact units, approximately thirty (30") inches in diameter for an eleven (11) MMScfd plant. Existing molecular sieve-based processes employ fixed beds in view of the possibility of sorbent attrition. The bubbling bed mode of operation (at about three (3) times the minimum fluidization velocity, with a minimum fluidization velocity of approximately thirty-three (33 fps) feet per second at one thousand (1000) psig and three hundred (300°) degrees K for molecular sieves with an average particle diameter of

approximately 0.06 inch) reduces the risk of attrition. In addition, a material, such as molybdenum sulfide, PTFE, graphite, among others, with a low coefficient of friction will be added to the bed in very small quantities to further reduce the potential for attrition.

The spent sorbent from the adsorber units is then pneumatically transported to the regeneration units. Regenerators are also operated in the bubbling fluidized bed mode; the temperature of operation is about four hundred and forty (440°) degrees F. The molecular sieve adsorbent from ADS1 is regenerated, with release of H<sub>2</sub>S and H<sub>2</sub>O, in RGN1. This unit is maintained in the bubbling fluidized bed mode using a slip stream from the partially-sweetened natural gas. Calculations show that about 0.5 (%) percent of the natural gas stream will suffice to maintain the operation of RGN1. The mixture of H<sub>2</sub>S, H<sub>2</sub>O, and natural gas recovered from RGN1 is used for the downstream recovery of elemental sulfur and hydrogen. Spent sorbent from ADS2 is regenerated, with release of CO<sub>2</sub>, in RGN2. The regenerated solids are recirculated into the adsorber units. The ease of sorbent transportation between adsorber and regeneration units is a key advantage of the process of the present invention (in comparison with other fixed dry bed processes) made possible by the use of the fluidized bed mode of operation.

The sorbent recirculation rates are determined by the amount of contaminants in the natural gas. Conventionally, gas-conditioning processes employing molecular sieves are based on fixed bed technology. Cooling and heating of beds to serve as adsorbers or regenerators requires time. The temperature swing adsorption then limits the region of operability to low H<sub>2</sub>S concentrations in medium scale operation. The ability to alter, with ease, the flow rate of solids within the adsorber and regenerator units through operation in the fluidized bed mode provides the process flexibility of operation in the handling of different compositions and greatly enhances the possible regime of operation in terms of H<sub>2</sub>S concentrations as well as processing scale. Since molecular sieves have a high surface area and, therefore, large adsorption capacities, the recirculation rate of solids is kept at a minimum, providing a compact design.

Energy is required to maintain the adsorber/regenerator loops operated on the principle of temperature swing adsorption. The energy to maintain the beds at four hundred and forty (440°) degrees F is supplied by combustion of gases in a pulse combustor, designated as PC2 and PC3 in FIG. 2, immersed within the gently bubbling fluidized beds. The submerged pulse combustors behave as submerged tubes and therefore deliver the well-known advantage of high heat transfer coefficients (thirty-five (35) to seventy (70) BTU hr<sup>-1</sup> ft<sup>-2</sup> °F<sup>-1</sup>) between the bed and the tubes. These heat transfer

coefficients are higher by, at least one order of magnitude in comparison with those obtained from a tube immersed in convective flow of a gas. The higher heat transfer coefficients make possible use of a lower surface area for heat exchange for the same temperature differences and heat duty resulting in a compact design fro the regenerator units. The mixing of solids within the bubbling bed ensures that the bed temperature is uniform. The fuel gas for the pulse combustors PC2 and PC3 submerged, respectively, in RGN1 and RGN2, is derived from the synthesis gas (CO and H<sub>2</sub>) generated in the corona reactor.

In a corona reactor, extremely reactive species, such as radicals and excited molecules are generated at ambient temperature without the presence of catalysts. Also, little energy is lost due to heating of the gas as compared with thermal processes.

The gas mixture, consisting of H<sub>2</sub>S and H<sub>2</sub>O released from the molecular sieves and natural gas used as the fluidization medium, from RGN1 is used for recovery of elemental sulfur and hydrogen. This recovery is effected in a pulsed corona reactor designated as PCR in FIG. 2. The gas mixture consisting of H<sub>2</sub>S, H<sub>2</sub>O, CH<sub>4</sub>, and CO<sub>2</sub>, following expansion, is introduced into the pulsed corona reactor where the following reactions take place:



The efficiency of sulfur recovery according to the present invention depends primarily on minimizing formation of CS<sub>2</sub> and COS in the corona reactor. By adjusting the amount of excess CO<sub>2</sub>, i.e., the H<sub>2</sub>S/CO<sub>2</sub> and CH<sub>4</sub>/CO<sub>2</sub> ratios, complete conversion of H<sub>2</sub>S and CH<sub>4</sub> is possible. Thus, in a nonthermal plasma reactor, H<sub>2</sub>S conversion exceeding ninety-nine (99%) percent is possible.

The gases exiting from the corona reactor consist, mainly, of unconverted H<sub>2</sub>S, CH<sub>4</sub>, and CO<sub>2</sub>, H<sub>2</sub>O, elemental sulfur species S; with I = 1 to 8, CO, H<sub>2</sub>, CS<sub>2</sub> and COS. These gases are quenched, in a condenser designated as COND in FIG. 2, to remove

elemental sulfur and water. The remaining gases -- H<sub>2</sub>S, CH<sub>4</sub>, CO<sub>2</sub>, CO, H<sub>2</sub>, CS<sub>2</sub>, and COS -- are compressed back to system pressure (1000 psig for the example considered) before flowing through an adsorption unit, designated as ADS3 in FIG. 2, where the gases also serve as the fluidizing medium for the bubbling bed. The adsorption unit removes H<sub>2</sub>S and CO<sub>2</sub> from the gas stream using the molecular sieve 5A. The spent sorbent from the adsorber unit is regenerated in RGN1 so that the unconverted H<sub>2</sub>S is recycled to the sulfur and hydrogen recovery pulsed corona reactor. The gases from ADS3, consisting of CH<sub>4</sub>, CO, H<sub>2</sub>, and COS, are passed through a hydrogen separation unit. The rest of the gas mixture is fired in pulse combustors PC2 and PC3, which provide the energy required to maintain the regenerators RGN1 and RGN2 at the temperature of four hundred and forty (440°) degrees F. It should be noted that a fraction of the gas stream exiting the hydrogen separator is used for fluidization of RGN2 after which the gases are fired in PC3. The off-gases from PC2 and PC3, following heat recovery, are vented.

10

15

In comparison with some of the existing processes, there are several advantages offered by the process configuration of the present invention including, but not limited to, recovery of elemental sulfur and hydrogen, smaller size and lower costs, energy efficiency, flexibility of operation for treatment of sour gas and Claus reactor effluent streams with varying H<sub>2</sub>S levels, etc.

20

First, concerning the recovery of elemental sulfur and hydrogen, the off-gas from the regenerator is sent to the flare in conventional fixed bed processes. In the system and process according to the present application, both elemental sulfur and hydrogen are recovered from H<sub>2</sub>S in the sour gas.

25

30

Second, the system and process according to the present invention provides smaller size and lower costs. Conventional technology employs fixed bed adsorption/ regeneration columns such that when the adsorber column gets exhausted, flow of "sour" gas is diverted to another adsorber column. The exhausted adsorber column is then regenerated by passage of hot gas. After regeneration, this column has to be cooled to the temperatures at which the molecular sieves will adsorb the contaminants again. Since the cooling of the bed takes time, conventional processes often require three (3) or four (4) columns. In the system and process of the present application, regenerated sorbent is recycled continuously. In addition, the thermal inertia and the excellent mixing characteristics in the two legs of the recirculating bed ensure that the temperatures are maintained at the levels required. Consequently, only two columns will be necessary.

Third, the system and process

according to the present invention provides

energy efficiency. In conventional processes, the energy required to raise the temperature of the molecular sieves to strip the contaminants is provided by combustion of a natural gas stream in a separate burner. The off-gases from the regenerator are sent to the flare. In this process, the synthesis gas generated from H<sub>2</sub>S in the corona reactor is burnt in pulse combustors and the regenerator is heated through the pulse combustors acting as immersed heat transfer tubes. Thus, the process makes use of the high heat transfer coefficients provided by submerged tubes in a fluidized bed. Also, the energy required to raise the bed temperature is obtained, indirectly, from H<sub>2</sub>S.

Finally, the system and process of the present application provides flexibility of operation. The sorbent recirculation rate can be adjusted to meet different levels of contamination in the natural gas. Calculations show that the process can sweeten sour gas of the composition (one (1%) percent H<sub>2</sub>S) with sulfur recovery of ninety-nine (99%) percent. The operating conditions identified by the thermodynamic calculations -- in terms of higher H<sub>2</sub>S/CO<sub>2</sub> ratios aiding higher sulfur recovery -- suggest that the proposed process can be used to advantage for conditioning of gas streams with higher H<sub>2</sub>S contents. Conventionally, gas-conditioning processes employing molecular sieves are based on fixed bed technology. Cooling and heating of beds to serve as adsorbers or regenerators requires time. The temperature swing adsorption then limits the region of operability to low H<sub>2</sub>S concentrations in medium scale operations. The ability to alter, with ease, the flow rate of solids within the adsorber and regenerator units through handling of different compositions and greatly enhances the possible regime of operation in terms of H<sub>2</sub>S concentrations as well as processing scale.

The foregoing exemplary descriptions and the illustrative preferred embodiments of the present invention have been explained in the drawings and described in detail, with varying modifications and alternative embodiments being taught. While the invention has been so shown, described and illustrated, it should be understood by those skilled in the art that equivalent changes in form and detail may be made therein without departing from the true spirit and scope of the invention, and that the scope of the present invention is to be limited only to the claims except as precluded by the prior art. Moreover, the invention as disclosed herein, may be suitably practiced in the absence of the specific elements which are disclosed herein.

CLAIMS

We claim:

1. A device for removing contaminants from a natural gas stream, the device comprising:

first adsorbent means positioned within a first fluidized bed operating at a first predetermined temperature for removing at least a portion of the contaminants from the natural gas stream and creating a partially sweetened natural gas stream; and

second adsorbent means positioned within a second fluidized bed operating at a second predetermined temperature for receiving the partially sweetened natural gas stream, the second adsorbent means removing at least a portion of the contaminants from the partially sweetened natural gas stream.

2. The device of claim 1 wherein the contaminants are selected from the group consisting of H<sub>2</sub>S, CO<sub>2</sub>, and H<sub>2</sub>O.

- 15 3. The device of claim 1 wherein the first adsorbent means is a molecular sieve.

4. The device of claim 1 wherein the second adsorbent means is a molecular sieve.

- 20 5. The device of claim 1 wherein the first predetermined temperature is greater than the second predetermined temperature.

6. The device of claim 1 wherein the first predetermined temperature is between approximately twenty (20°) degrees C and approximately sixty (60°) degrees C.

- 25 7. The device of claim 6 wherein the first predetermined temperature is approximately twenty-five (25°) degrees C.

- 30 8. The device of claim 1 wherein the second predetermined temperature is between approximately one hundred (100°) degrees C and approximately three hundred (300°) degrees C.

9. The device of claim 2 wherein the second predetermined temperature is approximately two hundred (200°) degrees C.

5 10. The device of claim 1 and further comprising:  
conversion means for converting H<sub>2</sub>S within the removed contaminants to elemental sulfur and hydrogen at a predetermined temperature less than approximately four hundred (400°) degrees C.

10 11. The device of claim 10 wherein the conversion means is a nonthermal plasma corona reactor.

12. An apparatus for converting H<sub>2</sub>S to elemental sulfur and hydrogen, the apparatus comprising:

15 conversion means for receiving H<sub>2</sub>S and for converting H<sub>2</sub>S to elemental sulfur and hydrogen at a predetermined temperature less than approximately four hundred (400°) degrees C.

20 13. The apparatus of claim 12 wherein the conversion means is a nonthermal plasma corona reactor.

14. The apparatus of claim 12 and further comprising:  
adsorbent means positioned within a fluidized bed for removing at least a portion of H<sub>2</sub>S from a natural gas stream; and  
means for providing the removed H<sub>2</sub>S to the conversion means.

25 15. The apparatus of claim 14 wherein the adsorbent means includes a first adsorbent having a first predetermined temperature and second adsorbent having a second predetermined temperature.

30

16. The apparatus of claim 15 wherein the first adsorbent means and the second adsorbent means are a molecular sieves.

17. The apparatus of claim 15 wherein the first predetermined temperature is

greater than the second predetermined temperature.

18. A method for removing H<sub>2</sub>S and other contaminants from a natural gas stream and converting H<sub>2</sub>S to elemental sulfur and hydrogen, the method comprising:

5 providing first adsorbent means;

positioning the first adsorbent means within a fluidized bed at a first predetermined temperature;

introducing the natural gas stream to the first adsorbent means thereby removing at least a portion of the H<sub>2</sub>S and other contaminants from the natural gas

10 stream and creating a partially sweetened natural gas stream;

providing second adsorbent means;

positioning the second adsorbent means within a fluidized bed at a second predetermined temperature;

introducing the partially sweetened natural gas stream to the second adsorbent means thereby removing at least a portion of the contaminants from the partially sweetened natural gas stream;

providing a nonthermal plasma reactor;

introducing the removed contaminants to the nonthermal plasma reactor; and converting the H<sub>2</sub>S to elemental sulfur and hydrogen at a third predetermined

20 temperature.

19. The method of claim 18 wherein the first adsorbent means and the second adsorbent means are molecular sieves.

25 20. The method of claim 18 wherein the first predetermined temperature being greater than the second predetermined temperature.

21. The method of claim 18 wherein the first predetermined temperature being between approximately twenty (20°) degrees C and approximately sixty (60°) degrees C.

30

22. The method of claim 18 wherein the second predetermined temperature being between approximately one hundred (100°) degrees C and approximately three hundred (300°) degrees C.

23. The method of claim 18 wherein the third predetermined temperature being less than approximately four hundred (400°) degrees C.

Fig. 1

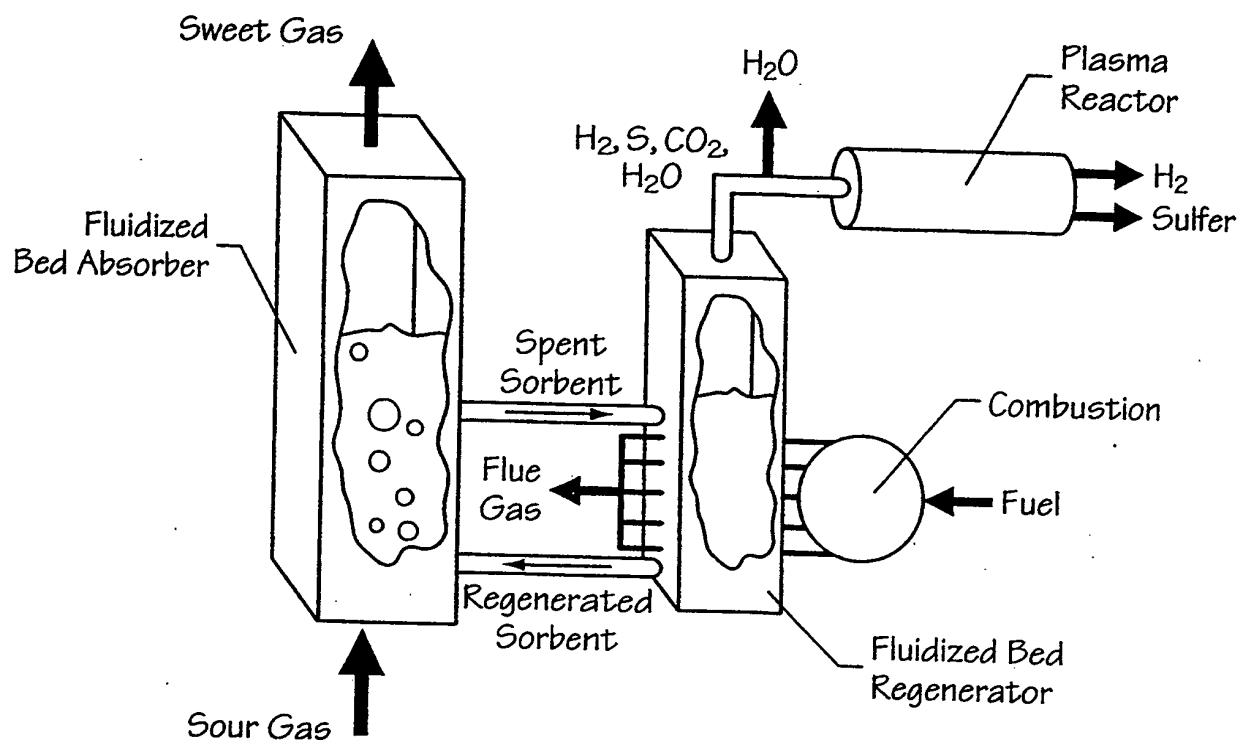
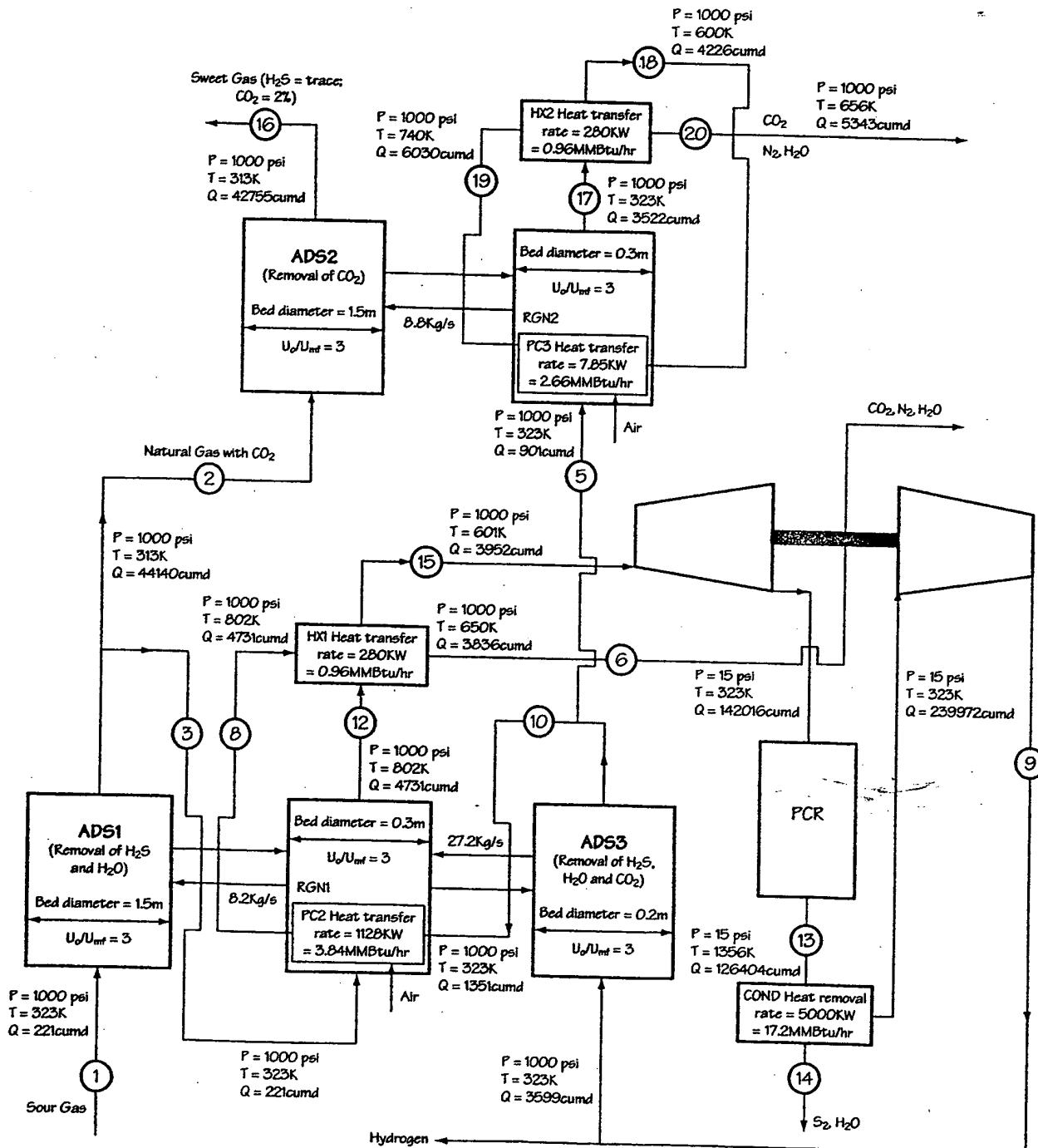


Fig. 2



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/07753

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :B01J 8/18, 8/26; C10L 3/10; H05H 1/00  
US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 48/127.3, 127.5, 127.9, 128; 95/117, 136, 139; 204/164; 423/230, 573.1, DIG. 10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HARKNESS, J. B. L. et al. "Hydrogen Sulfide Waste Treatment by Microwave Plasma Dissociation" presented at the 25th Intersociety Energy Conversion Engineering Conference in Reno, Nevada USA, August 12-17, 1990, pgs. 197-202.	12-13
Y	CA 675,292 A (MILTON) 03 December 1963, pg. 13 lns. 12-21, pg. 14 ln. 19 to pg. 19 ln. 8 and the claims.	10-14, 18, 23
A	HELFritch, "Pulsed Corona Discharge for Hydrogen Sulfide Decomposition", IEEE Transactions on Industry Applications, Vol. 29, No. 5, Septemeber/October 1993, pgs. 882-886.	10-14, 18, 23

Further documents are listed in the continuation of Box C.  See patent family annex.

Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"		document defining the general state of the art which is not considered to be of particular relevance
"E"	"X"	earlier document published on or after the international filing date
"L"		document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	"Y"	document referring to an oral disclosure, use, exhibition or other means
"P"	"Z"	document published prior to the international filing date but later than the priority date claimed

Date of the actual completion of the international search  02 MAY 2000	Date of mailing of the international search report  25 MAY 2000
--	---

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington D.C. 20231

Authorized officer  
*[Signature]*  
DEBORAH THOMAS  
TIMOTHY C. VANOY PARALEGAL SPECIALIST

**INTERNATIONAL SEARCH REPORT**International application No.  
PCT/US00/07753

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,520,894 A (HEESINK et al.) 28 May 1996, col. 3 ln. 47 to col. 4 ln. 19 and Fig. 1.	1-9 and 14-22
A	US 5,211,923 A (HARKNESS et al.) 18 May 1993, col. 1 lns. 61-67, col. 2 ln. 43 to col. 3 ln. 13 and Fig. 1.	10-14, 18, 23
A	US 4,358,297 A (EBERLY, JR.) 09 November 1982, claims 1-9.	1-9 and 14-22

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/07753

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,520,894 A (HEESINK et al.) 28 May 1996, col. 3 ln. 47 to col. 4 ln. 19 and Fig. 1.	1-9 and 14-22
A	US 5,211,923 A (HARKNESS et al.) 18 May 1993, col. 1 lns. 61-67, col. 2 ln. 43 to col. 3 ln. 13 and Fig. 1.	10-14, 18, 23
A	US 4,358,297 A (EBERLY, JR.) 09 November 1982, claims 1-9.	1-9 and 14-22

**INTERNATIONAL SEARCH REPORT**

International application No.  
PCT/US00/07753

**A. CLASSIFICATION OF SUBJECT MATTER:**  
**US CL :**

**48/127.3, 127.5, 127.9, 128; 95/117, 136, 139; 204/164; 423/230, 573.1, DIG. 10**